

PCT

COMMUNICATION OF  
INTERNATIONAL APPLICATIONS

(PCT Article 20)

From the INTERNATIONAL BUREAU

To:

United States Patent and Trademark  
Office  
Attention: Box PCT  
Room 3A01, South Tower  
2900 Crystal Drive  
Arlington, VA 22202  
United States of America

in its capacity as designated Office

Date of mailing:

20 May 2005 (20.05.2005)

The International Bureau transmits herewith copies of the international applications having the following international application numbers and international publication numbers:

International application no.:

PCT/JP2003/009548

International publication no.:The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer:

Yoshiko KUWAHARA (Fax 338 9090)

Telephone No.: (41-22) 338.83.38

(corresponding to page 6 to page 8)

or the alloy composed of at least two kinds of those metals.

5

#### Disclosure of Invention

Therefore, an object of the present invention is to stably form carbon nanotubes patterned in the shape based on the design on a substrate surface.

Also, another object of the present invention  
10 is to improve an adhesive property of a catalyst containing film to a substrate.

Still another object of the present invention is to improve a patterning property of the catalyst containing film.

15

Still another object of the present invention is to provide a technique for generating the carbon nanotubes, especially, the single-wall carbon nanotubes extended in a direction horizontal to the substrate, at a high yield.

20

Still another object of the present invention is to provide an electronic element such as a transistor, which is excellent in high-speed operation property and high-integrated property, by using the carbon nanotubes.

25

In order to achieve an aspect of the present invention, the present invention provides a catalyst supporting substrate including: a first

region which is formed on a substrate; and a second region which is formed covering a part of the first region. The first region includes a catalyst supporting portion containing a first material.

5 The second region includes a catalyst portion containing a second material which is different from the first material. The first material includes a metal containing at least one of elements selected from the second group to the fourteenth group of the

10 periodic table or a compound thereof. The second material is a catalyst which grows carbon nanotubes in a vapor phase.

In the catalyst supporting substrate, the carbon nanotubes include single-wall carbon

15 nanotubes.

In the catalyst supporting substrate, the second material includes a metal containing at least one of elements selected from a group consisting of Fe, Ni, Co, Ru, Rh, Pd, Os, Ir, Pt, La, Y, Mo and

20 Mn or a compound thereof.

In the catalyst supporting substrate, the first material includes a metal containing at least one of elements selected from a group consisting of Al, Mo, Ti, Ta, Cr, Cu, Mn, Mg, Zr, Hf, W, Ru, Rh,

25 Zn and Sn or a compound thereof.

In the catalyst supporting substrate, the first region includes a metal film which contains

the first material and is formed on the substrate. The catalyst supporting portion includes a film that an upper portion of the metal film is oxidized or hydroxylated.

5           In the catalyst supporting substrate, the second material includes a metal containing at least one of elements selected from a group consisting of Fe, Ni, Co, Ru, Rh, Pd, Os, Ir, Pt, La, Y, Mo and Mn or a compound thereof.

10           In the catalyst supporting substrate, the first material includes a metal containing at least one of elements selected from a group consisting of Al, Mo, Ti, Ta, Cr, Cu, Mn, Mg, Zr, Hf, W, Ru, Rh, Zn and Sn or a compound thereof.

15           In the catalyst supporting substrate, a surface of the catalyst supporting portion includes at least one selected from aluminum natural oxide film, boehmite,  $\alpha$  alumina,  $\gamma$  alumina,  $\delta$  alumina, and  $\theta$  alumina.

20           In order to achieve another aspect of the present invention, the present invention provides a transistor including: a catalyst, the carbon nanotubes, a first electrode, a second electrode and a gate electrode. The catalyst containing film is  
25 placed on a substrate and grows carbon nanotubes in a vapor phase. The carbon nanotubes are extended in the direction along a surface of the substrate

from the catalyst containing film. The first electrode is connected to a part of the catalyst containing film side of the carbon nanotubes. The second electrode is connected to a part of another  
5 side of the carbon nanotubes. The gate electrode applies a voltage to the carbon nanotubes between the first electrode and the second electrode.

In the transistor, the carbon nanotubes includes single-wall carbon nanotubes.

10 In the transistor, the gate electrode is placed on an upper portion of the carbon nanotubes.

In the transistor, the gate electrode is placed on a rear surface of the substrate.

In the transistor, the second electrode is  
15 formed so as to be separated from the first electrode and surround a periphery of the first electrode.

In the transistor, the catalyst containing film includes: a first region which is formed on a substrate; and a second region which is formed  
20 covering a part of the first region. The first region includes a catalyst supporting portion containing a first material. The second region includes a catalyst portion containing a second material which is different from the first material.  
25 The first material includes a metal containing at least one of elements selected from the second group to the fourteenth group of the periodic table or a

compound thereof. The second material is a catalyst which grows carbon nanotubes in a vapor phase.

In the transistor, the second material includes a metal containing at least one of elements  
5 selected from a group consisting of Fe, Ni, Co, Ru, Rh, Pd, Os, Ir, Pt, La, Y, Mo and Mn or a compound thereof.

In the transistor, the first material includes a metal containing at least one of elements selected  
10 from a group consisting of Al, Mo, Ti, Ta, Cr, Cu, Mn, Mg, Zr, Hf, W, Ru, Rh, Zn and Sn or a compound thereof.

In the transistor, the first region includes a metal film which contains the first material and  
15 is formed on the substrate. The catalyst supporting portion includes a film that an upper portion of the metal film is oxidized or hydroxylated.

In the transistor, the second material includes a metal containing at least one of elements  
20 selected from a group consisting of Fe, Ni, Co, Ru, Rh, Pd, Os, Ir, Pt, La, Y, Mo and Mn or a compound thereof.

In the transistor, the first material includes a metal containing at least one of elements selected  
25 from a group consisting of Al, Mo, Ti, Ta, Cr, Cu, Mn, Mg, Zr, Hf, W, Ru, Rh, Zn and Sn or a compound thereof.

In order to achieve still another aspect of the present invention, the present invention provides a method for growing carbon nanotubes including:

(a) providing a catalyst supporting substrate;  
5 and (b) growing the carbon nanotubes by supplying raw material gas containing carbon to a catalyst supporting substrate. The catalyst supporting substrate includes: a first region which is formed on a substrate; and a second region which is formed  
10 covering a part of the first region. The first region includes a catalyst supporting portion containing a first material. The second region includes a catalyst portion containing a second material which is different from the first material.  
15 The first material includes a metal containing at least one of elements selected from the second group to the fourteenth group of the periodic table or a compound thereof. The second material is a catalyst which grows carbon nanotubes in a vapor phase.

20 In the method for growing carbon nanotubes, the carbon nanotubes include single-wall carbon nanotubes.

In the method for growing carbon nanotubes, the step (b) includes: (b1) growing the carbon nanotubes  
25 in the direction along a surface of the catalyst supporting substrate.

In the method for growing carbon nanotubes, the

step (b1) includes: (b11) applying an electric field with the predetermined direction to the catalyst supporting substrate.

5 In the method for growing carbon nanotubes, the step (b) includes: (b2) bringing reducing gas into contact with a surface of the catalyst supporting substrate.

10 In the method for growing carbon nanotube, the step (a) includes: (a1) forming the first region and the second region which are patterned with predetermined shapes on the substrate.

In the method for growing carbon nanotubes, the carbon nanotubes include single-wall carbon nanotubes.

15 In the method for growing carbon nanotubes, the second material includes a metal containing at least one of elements selected from a group consisting of Fe, Ni, Co, Ru, Rh, Pd, Os, Ir, Pt, La, Y, Mo and Mn or a compound thereof.

20 In the method for growing carbon nanotubes, the first material includes a metal containing at least one of elements selected from a group consisting of Al, Mo, Ti, Ta, Cr, Cu, Mn, Mg, Zr, Hf, W, Ru, Rh, Zn and Sn or a compound thereof.

25 In the method for growing carbon nanotubes, the step (a1) includes: (a11) forming a catalyst supporting portion which are patterned with



predetermined shape on the substrate, and (a12) forming a catalyst portion which covers a part of a surface of the catalyst supporting portion.

In the method for growing carbon nanotubes, the  
5 step (a11) includes: (a111) forming a metal film which contains at least one of elements selected from the second group to the fourteenth group

(corresponding to page 10)

Also, the method for growing the carbon nanotubes according to the present invention can stably obtain the carbon nanotubes of the high  
5 quality, especially, the single-wall carbon nanotubes at the high yield. The obtained carbon nanotubes are excellent in the adhesive property to the substrate and can be preferably applied to the electronic device, such as the transistor excellent  
10 in the high-speed operation property and high-integrated property and the like.

Also, the transistor according to the present invention is excellent in the adhesive property between the carbon nanotubes and the electrodes.  
15 When the carbon nanotubes are assumed to be the single-wall carbon nanotubes, the device property excellent in the high-speed operation property can be stably obtained. In addition, since the channel current flowing through the carbon nanotubes is  
20 largely changed by applying voltage, the ideal transistor can be obtained.

Moreover, the method for manufacturing the transistor according to the present invention, can obtain the transistor having the excellent high  
25 speed operation property and high reliability at the excellent manufacturing stability, since forming the carbon nanotube portion by using the method for

growing the carbon nanotubes as mentioned above.

In the present invention, since both of the catalyst film and the catalyst support film can be easily patterned by etching, the device of the  
5 desired shape can be formed at the good yield.

### Brief Description of Drawings

Fig. 1 is a flowchart showing a film forming process of the method for growing the carbon  
10 nanotubes in the first embodiment of the present invention;

Fig. 2A to Fig. 2E are sectional views showing an example of the film forming process in Fig. 1;

Fig. 3A and Fig. 3B are views showing one  
15 example of the structure of the transistor using the carbon nanotubes in the second embodiment of the present invention;

Fig. 4A and Fig. 4B are views showing another example of the structure of the transistor using the  
20 carbon nanotubes in the second embodiment of the present invention;

Fig. 5A and Fig. 5B are views showing still another example of the structure of the transistor using the carbon nanotubes in the second embodiment  
25 of the present invention;

Fig. 6 is a top view showing another example of the structure of the transistor using the carbon

nanotubes in the second embodiment of the present invention;

Fig. 7 is a top view showing still another example of the structure of the transistor using the  
5 carbon nanotubes in the second embodiment of the present invention;

Fig. 8A to Fig. 8D, Fig. 9A to Fig. 9D and Fig. 10A to Fig. 10D are sectional views showing the method for manufacturing the transistor shown in Fig.  
10 3A and Fig. 3B;

Fig. 11 is a photograph of the scanning electron microscope, showing the generated sediment in the example;

Fig. 12 is a photograph of the transmission  
15 electron microscope, showing the sediment shown in Fig. 11;

(corresponding to page 18 to page 20)

The using the above-mentioned patterned catalyst and catalyst support enables the selective growth of the single-wall carbon nanotubes. However, the direction of the single-wall carbon nanotubes manufactured at that time is random. It is known that the application of the external field, such as electric field, magnetic field or the like, to the single-wall carbon nanotubes makes the directions equal. Even in the above-mentioned patterned catalyst and catalyst support, the directions can be made equal by applying the external field, such as the electric field, the magnetic field, or the centrifugal force when the substrate is rotated, or the like, when the carbon material is supplied.

[Second Embodiment]

The second embodiment of the present invention will be described below with reference to the attached drawings. This embodiment relates to the transistor using the carbon nanotubes in the present invention.

Fig. 3A and Fig. 3B are views showing one example of the structure of the transistor using the carbon nanotubes in the second embodiment of the present invention. Fig. 3B shows a top view of the transistor. Fig. 3A shows a sectional view along

the line AA' of Fig. 3B. The transistor in this embodiment has the structure that a silicon oxide film 2 is formed on a silicon substrate 1, and a device portion is formed thereon. The device  
5 portion includes: a gate electrode composed of an insulating film 19 and a gate metal film 20; a source electrode 30 and a drain electrode 31 which are formed on both sides thereof; and a carbon nanotubes  
10 5 for connecting them. The carbon nanotubes 5 are grown in the direction parallel to the substrate surface from a catalyst film 40 formed on a catalyst support film 4 (containing a catalyst support layer 4a and a foundation layer 4b). In this transistor, the carbon nanotubes 5 are responsible for a role  
15 as a channel region. That is, when a voltage is applied to the gate electrode composed of the insulating film 19 and the gate metal film 20, the conductive property of the carbon nanotubes 5 is changed. Thus, a current flowing between the source  
20 electrode 30 and the drain electrode 31 is changed.

Fig. 4A and Fig. 4B are views showing another example of the structure of the transistor using the carbon nanotubes in the second embodiment of the present invention. Fig. 4B shows a top view of the  
25 transistor. Fig. 4A shows a sectional view along the line BB' of Fig. 4B. This transistor has the structure schematically similar to the transistor

shown in Fig. 3A and Fig. 3B. However, it is different in point that the insulating film 19 and the gate metal film 20 are formed so as to sit astride the source electrode 30 and the drain electrode 31.

5        Fig. 5A and Fig. 5B are views showing still another example of the structure of the transistor using the carbon nanotubes in the second embodiment of the present invention. Fig. 5B is a top view of the transistor. Fig. 5A shows a sectional view  
10 along the line CC' of Fig. 5B. This transistor is the transistor of a so-called back gate type. Differently from the transistors of Fig. 3A and Fig. 3B and Fig. 4A and Fig. 4B, a gate electrode 21 is formed on the rear of the silicon substrate 1. In  
15 this transistor, the gate electrode 21 is formed at the position away from the carbon nanotubes 5. Thus, the formation of the gate electrode is easy.

In the present invention, the source electrode and the drain electrode may be variously arranged.

20        Fig. 6 is a top view showing another example of the structure of the transistor using the carbon nanotubes in the second embodiment of the present invention. In this transistor, the arrangements of the source electrode 30 and the drain electrode 31  
25 are different from the transistors in Fig. 3A and Fig. 3B to Fig. 5A and Fig. 5B. The drain electrode 31 is formed so as to be separated from the source

electrode 30 and surround a part of the periphery of the source electrode 30. The gate metal film 20 is formed in the region between the source electrode 30 and the drain electrode 31. The carbon nanotubes 5 are formed so as to sit astride the source electrode 30 and the drain electrode 31. These carbon nanotubes 5 are grown in vapor phase in the direction parallel to the surface of the substrate with the catalyst support film 4 as a start point. Since the source electrode 30 and the drain electrode 31 are arranged as mentioned above, the connection through the carbon nanotubes 5 between both of the electrodes can be surely attained. That is, when the carbon nanotubes 5 are grown in the vapor phase with the catalyst support film 4 as the start point, the direction of the growth can be all directions within the surface plane. In the case of employing the arrangement of Fig. 6, even if the growth direction of the carbon nanotubes 5 are fluctuated in various directions, the source electrode 30 and the drain electrode 31 can be surely connected through the carbon nanotubes 5.

Fig. 7 is a top view showing still another example of the structure of the transistor using the carbon nanotubes in the second embodiment of the present invention. In this transistor, the arrangements of the source electrode 30 and the



drain electrode 31 are different from the transistors in Fig. 3A and Fig. 3B to Fig. 6. In this arrangement, around the source electrode 30, the drain electrode 31 is formed so as to be separated  
5 from the source electrode 30 and surround the periphery of the source electrode 30. The gate metal film 20 is formed between the source electrode 30 and the drain electrode 31. The carbon nanotubes 5 are formed so as to be connected to both of the  
10 source electrode 30 and the drain electrode 31. This carbon nanotubes 5 are grown in the direction parallel to the surface of the substrate with the catalyst support film 4 as the start point. In the case of employing this arrangement, even if the  
15 carbon nanotubes 5 are grown in any direction, the electric connection between the source electrode 30 and the drain electrode 31 can be attained. Here, since the distance between the source electrode 30 and the drain electrode 31 is suitably set by  
20 considering the growth condition of the carbon nanotubes 5, the electric connection through a carbon nanotubes 5 can be made further sure.

In the transistor as mentioned above, the source electrode 30 and the drain electrode 31 can  
25 be the single-wall film made of gold, platinum, titanium and the like or the lamination film of them. As a gate metal film 20, at least one kind of metals,

such as aluminum, gold, titanium and tungsten and the like, can be used.

One example of a method for manufacturing the transistor shown in Fig. 3A and Fig. 3B will be  
5 described below.

Fig. 8A to Fig. 8D, Fig. 9A to Fig. 9D and Fig. 10A to Fig. 10D are sectional views showing the method for manufacturing the transistor shown in Fig. 3A and Fig. 3B.

10 At first, the silicon oxide film 2 and a catalyst support material (the first metal film) 3 are formed on the silicon substrate 1, as shown in Fig. 8A. The catalyst support material 3 has the structure in which TiN, aluminum and aluminum oxide  
15 are laminated in this order. The TiN is used as the adhesive film to improve the adhesive property between the silicon oxide film 2 and the aluminum thereon.

In succession, after mask is formed on the  
20 catalyst support material 3, the dry etching is carried out to pattern the catalyst support material 3 and form the catalyst support film 4. In this case, the catalyst support layer 4a is aluminum oxide. The foundation layer 4b is TiN and aluminum. The  
25 catalyst film 40 having iron (Fe) is formed on this catalyst support film 4 by using the depositing method. The film thickness of the catalyst film 40

is about 2 to 5 nm. The design of such film thickness enables the configuration that the catalyst film 40 is interspersed on a part of the surface of the catalyst support film 4. That is, the structure, in which both of the catalyst support film 4 and the catalyst film 40 are exposed, can be attained. Incidentally, here, the iron (Fe) is used as the material of the catalyst film 40. However, as mentioned above, the material other than this can be used. This situation is shown in Fig. 8B.

Next, the silicon substrate 1 is placed in a CVD film forming chamber. After that, the raw material gas, such as methane, acetylene and the like, is supplied to the silicon substrate 1. Thus, the carbon nanotubes 5 is grown in vapor phase from the catalyst film 40. The carbon nanotubes 5 are extended in the direction approximately parallel to the surface of the substrate. This situation is shown in Fig. 8C. In order to extend the carbon nanotubes 5 having the single-wall structure in the direction approximately parallel to the surface of the substrate, it is important to properly select the materials of the catalyst film 40 and support thereof and growth temperatures.

In succession, a resist 6 is formed so as to cover the catalyst support film 4 and the catalyst film 40. This situation is shown in Fig. 8D.

Next, as shown in Fig. 9A, the resist 6 is exposed through a mask 8 in which an opening is placed. Thus, a dissolvable region 10 dissolved in development solution is formed.

5        In succession, by processing the resist 6 surface with the predetermined solution such as monochloro-benzene, a resist deterioration layer 12 which is difficult to dissolve in the development solution is formed. This situation is shown in Fig.  
10    9B.

After that, the dip in the development solution causes the

CLAIMS:

(corresponding to page 26 and page 27)

1. (amended) A catalyst supporting substrate  
5 comprising:

a first region which is formed on a substrate;  
and

a second region which is formed covering a part  
of said first region;

10 wherein said first region includes:

a catalyst supporting portion containing a  
first material, and

a metal film which contains said first  
material,

15 said second region includes a catalyst portion  
containing a second material which is different from  
said first material,

said first material includes a metal  
containing one of Al and Si or a compound thereof,

20 said second material is a catalyst which grows  
carbon nanotubes in a vapor phase, and

said catalyst supporting portion includes a  
film that an upper portion of said metal film is  
oxidized or hydroxylated.

25

2. The catalyst supporting substrate according to  
claim 1, wherein said carbon nanotubes include

single-wall carbon nanotubes.

3. (canceled)

5 4. (canceled)

5. (canceled)

6. The catalyst supporting substrate according to  
10 claim 1,

wherein said second material includes a metal  
containing at least one of elements selected from  
a group consisting of Fe, Ni, Co, Ru, Rh, Pd, Os,  
Ir, Pt, La, Y, Mo and Mn or a compound thereof.

15

7. (canceled)

8. The catalyst supporting substrate according to  
claim 7, wherein a surface of said catalyst  
20 supporting portion includes at least one selected  
from aluminum natural oxide film, boehmite,  $\alpha$   
alumina,  $\gamma$  alumina,  $\delta$  alumina, and  $\theta$  alumina.

9. (amended) A transistor comprising:

25 a catalyst containing film which is placed on  
a substrate and grows carbon nanotubes in a vapor  
phase;

said carbon nanotubes which are extended in the direction along a surface of said substrate from said catalyst containing film;

5 a first electrode which is connected to a part of said catalyst containing film side of said carbon nanotubes;

a second electrode which is connected to a part of another side of said carbon nanotubes; and

10 a gate electrode which applies a voltage to said carbon nanotubes between said first electrode and said second electrode,

wherein said catalyst containing film includes:

15 a first region which is formed on a substrate; and

a second region which is formed covering a part of said first region;

wherein said first region includes:

20 a catalyst supporting portion containing a first material, and

a metal film which contains said first material,

25 said second region includes a catalyst portion containing a second material which is different from said first material,

said first material includes a metal containing one of Al and Si or a compound thereof,

said second material is a catalyst which grows carbon nanotubes in a vapor phase, and

(corresponding to page 29)

5 18. The transistor according to claim 9, wherein said second material includes a metal containing at least one of elements selected from a group consisting of Fe, Ni, Co, Ru, Rh, Pd, Os, Ir, Pt, La, Y, Mo and Mn or a compound thereof.

10

19. (canceled)

20. (amended) A method for growing carbon nanotubes comprising:

15 (a) forming a metal film by using a first material containing one of Al and Si;

(b) forming a catalyst supporting portion by oxidizing or hydroxylating an upper portion of said metal film;

20 (c) forming a catalyst portion containing a second material which is different from said first material such that said catalyst portion covers a part of a surface of said catalyst supporting portion; and

25 (d) growing said carbon nanotubes by supplying raw material gas containing carbon to a catalyst portion,



wherein said second material is a catalyst  
which grows carbon nanotubes in a vapor phase.

21. The method for growing carbon nanotubes  
5 according to claim 20, wherein said carbon nanotubes  
include single-wall carbon nanotubes.

22. The method for growing carbon nanotubes  
according to claim 20, wherein said step (d)  
10 includes:

(d1) growing said carbon nanotubes in the  
direction along